Supporting information for:

DFT Mechanistic Study on Methane mono-esterification by Hypervalent Iodine Alkane Oxidation Process

Ross Fu[†], Robert J. Nielsen[†], Nichole S. Liebov[‡], William A. Goddard III[†*], T. Brent Gunnoe[‡], John T. Groves[§]

[†]Materials and Process Simulation Center (139-74), California Institute of Technology, Pasadena, CA 91125, USA

[‡]Department of Chemistry, University of Virginia, Charlottesville, VA 22904, USA

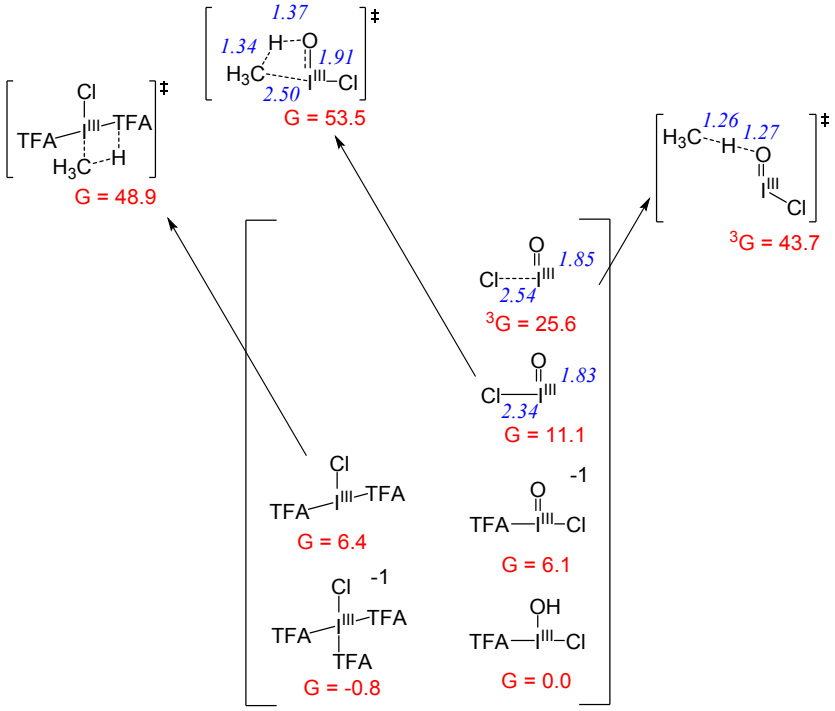
[§]Department of Chemistry, Princeton University, Princeton, NJ 08544, USA

Experimental details for a representative reaction of KCl/NH_4IO_3 in acetic acid with methane or argon

A VCO reactor was charged with a stir bar, 0.67 mmol KCl, 7.7 mmol of NH_4IO_3, and 8 mL HOAc. The reactor was sealed and weighed prior to pressurizing with 500 psi of the appropriate gas (37 mmol CH_4 or 11 mmol Ar). Subsequently, the reactor was weighed to determine the amount of added gas. It was then heated at 200 °C in an aluminum block for 1 h while stirring at 800 rpm. After 1 h, the reactor was removed from heat and allowed to cool in front of a fan for 30 min. The reactor was weighed to ensure that it did not leak during the course of the reaction. After opening the reactor, 30 μL of CH_3NO_2 was added to the reaction mixture as an internal standard, and the mixture was stirred. An aliquot was removed and centrifuged. The supernatant liquid was analyzed by ^{1}H NMR spectroscopy. ^{1}H NMR δ 3.64 (3H, H_3C-O_2CCH_3), 2.02 (3H, H_3C-O_2CCH_3, overlaps with HOAc). In a typical reaction with acetic acid-d_4, the reactions were scaled down (0.12 mmol KCl, 1.4 mmol NH_4IO_3, 1.5 mL acetic acid-d_4) but otherwise performed as indicated above. The reaction mixtures were then analyzed by ^{1}H NMR and GC-MS.

Additional figures, schemes, and tables

Scheme S1. Possible I(III) intermediates and transition states for non-radical and radical CH_4-activation pathways. Free energies in kcal/mol.



Note these free energies were calculated slightly differently than those in the text. Geometries were optimized including implicit solvation using the M06-2X functional and basis sets cc-pvtz-pp (I), 6-311++G-3df-3pd (Cl) and 6-311G**++ (other elements). 1M chloride (aq) and liquid water were used as reference states. Bond lengths in Ångstroms are in blue. Superscript "3" denotes a triplet state.

Table S1. Relative enthalpies and free energies of I(V) species with oxo, hydroxo, TFA, and chloro ligands[a]

Cl	TFA	H_2O[b]	Species	H (base[a])	G (base[a])	H (acid[a])	G (acid[a])	Geometry notes[c]
0	0	0	HIO_3	0	0	0	0	TPy
			IO_3^-	−0.3	2.4	3.0	5.7	TPy
		1	H_3IO_4	−0.5	10.5	−0.5	10.5	SS; oxo eq.
			$H_2IO_4^-$	−2.3	11.4	1.0	14.7	SS; oxos eq.
		2	H_5IO_5	−5.7	23.5	−5.7	23.5	SPy
			$H_4IO_5^-$	1.4	29.2	4.6	32.5	SPy; oxo ax.
	1	0	IO_2TFA	10.0	12.8	10.0	12.8	TPy
		1	$IO(OH)_2TFA$	−9.7	8.4	−9.7	8.4	SS; oxo eq., TFA ax.
			$IO_2(OH)TFA^-$	−12.5	2.6	−9.2	5.9	SS; oxos eq.
		2	$I(OH)_4TFA$	−12.5	20.1	−12.5	20.1	SPy; TFA eq.
			$IO(OH)_3TFA^-$	−2.3	30.0	1.0	33.2	SPy; oxo, TFA, eq.
	2	0	$IO(OH)(TFA)_2$	−2.5	18.5	−2.5	18.5	SS; TFAs ax.
		1	$I(OH)_3(TFA)_2$	−20.2	15.5	−20.2	15.5	SPy; TFAs eq.
			$IO(OH)_2(TFA)_2^-$	−30.6	4.3	−27.4	7.6	SPy; oxo ax. TFAs eq.
	3	0	$IO(TFA)_3$	11.5	35.1	11.5	35.1	SS; oxo ax.
		1	$I(OH)_2(TFA)_3$	−2.9	36.2	−2.9	36.2	SPy; TFAs eq.
	4	0	$I(OH)(TFA)_4$	7.3	49.5	7.3	49.5	SPy; oxo ax.
	5	0	$I(TFA)_5$	25.0	71.4	25.0	71.4	SPy

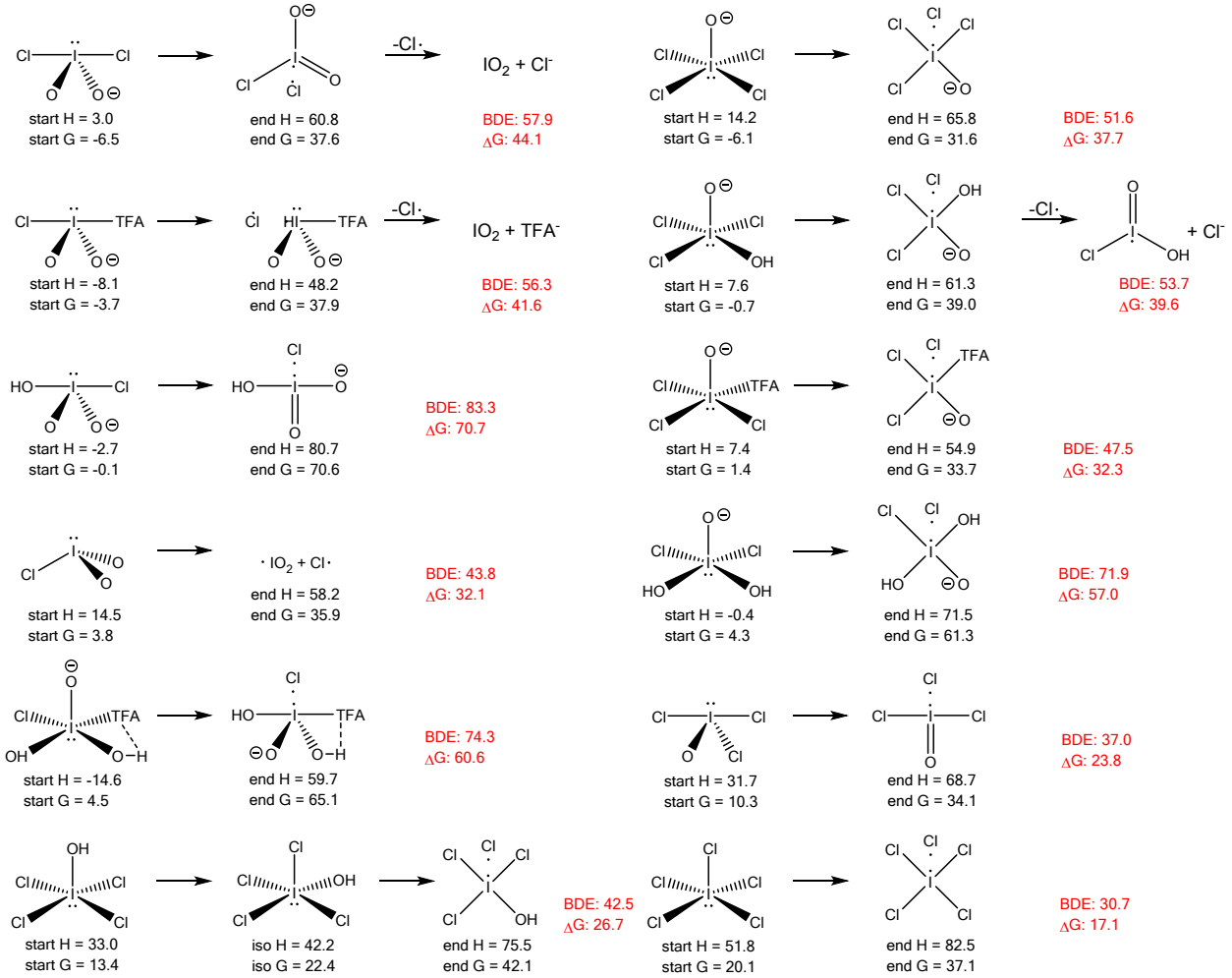
1	0	0	IO_2Cl	14.5	3.8	11.2	0.5	TPy
		1	$IO(OH)_2Cl$	2.9	6.4	−0.4	3.1	SS; Cl ax., oxo eq.
			$IO_2(OH)Cl^-$	−2.7	−0.1	−2.7	−0.1	SS; oxos eq.
		2	$I(OH)_4Cl$	1.6	18.9	−1.6	15.6	SPy; Cl eq.
			$IO(OH)_3Cl^-$	0.7	17.2	0.7	17.2	SPy; Cl eq. oxo ax.
	1	0	IO(OH)ClTFA	6.4	12.0	3.2	8.9	SS; oxo, OH eq.
			IO_2ClTFA^-	−8.1	−3.7	−8.1	−3.7	SS; oxos eq.
		1	$I(OH)_3ClTFA$	−0.5	19.5	−3.8	16.2	SPy; Cl, TFA eq.
			$IO(OH)_2ClTFA^-$	−14.6	4.5	−14.6	4.5	SPy; Cl, oxo, TFA eq.
	2	0	$IOCl(TFA)_2$	17.9	25.8	14.6	22.5	SS; TFAs ax.
		1	$I(OH)_2Cl(TFA)_2$	8.0	31.2	4.7	28.0	SPy; TFAs, Cl eq.
	3	0	$I(OH)Cl(TFA)_3$	20.7	47.5	17.4	44.2	SPy; TFAs, Cl eq.
	4	0	$ICl(TFA)_4$	30.5	60.6	27.2	57.3	SPy; Cl eq.
2	0	0	$IO(OH)Cl_2$	14.9	6.1	8.3	−0.5	SS; Cls ax.
			$IO_2Cl_2^-$	3.0	−6.5	−0.3	−9.7	SS; Cls ax.
		1	$I(OH)_3Cl_2$	10.3	14.9	3.7	8.3	SPy; Cls eq.
			$IO(OH)_2Cl_2^-$	−0.4	4.3	−3.7	1.0	SPy; Cls eq., oxo ax.
	1	0	$IOCl_2TFA$	29.0	21.2	22.5	14.7	SS; Cls ax.
		1	$I(OH)_2Cl_2TFA$	8.8	17.1	2.2	10.5	SPy; Cls, TFA eq.
			$IO(OH)Cl_2TFA^-$	0.5	6.8	−2.8	3.5	SPy; oxo ax.
	2	0	$I(OH)Cl_2TFA_2$	23.2	33.9	16.6	27.4	SPy; OH ax.
	3	0	ICl_2TFA_3	38.5	52.3	31.9	45.8	SPy; Cls eq.
3	0	0	$IOCl_3$	31.7	10.3	21.9	0.5	SS; oxo ax.
		1	$I(OH)_2Cl_3$	31.3	23.9	21.5	14.1	SPy; OHs eq.
			$IO(OH)Cl_3^-$	7.6	−0.7	1.0	−7.2	SPy; oxo ax.
	1	0	$I(OH)Cl_3TFA$	24.0	20.2	14.2	10.4	SPy; OH ax.
			$IOCl_3TFA^-$	7.4	1.4	0.9	−5.1	SPy; oxo ax.
	2	0	ICl_3TFA_2	39.4	37.2	29.5	27.3	SPy; TFAs eq.
4	0	0	$I(OH)Cl_4$	33.0	13.4	19.9	0.4	SPy; OH ax.
			$IOCl_4^-$	14.2	−6.1	4.4	−15.9	SPy; oxo ax.
	1	0	ICl_4TFA	47.2	30.5	34.0	17.4	SPy; TFA eq.
5	0	0	ICl_5	51.8	20.1	35.4	3.7	SPy

[a]All numbers in kcal/mol. Energies in basic solution are relative to HIO_3, I_2Cl^-, I_2, H_2O, TFAH, and TFA^-. Energies in acidic solution are relative to HIO_3, I_2Cl^-, I_2, H_2O, TFAH, H_2SO_4, and HSO_4^-.

[b]H_2O count refers to number of H_2O molecules that could theoretically be removed from species. For example, a count of 0 means that the species has no more than 1 hydroxo ligand; a count of 1 means 2-3 hydroxo ligands, and so on.

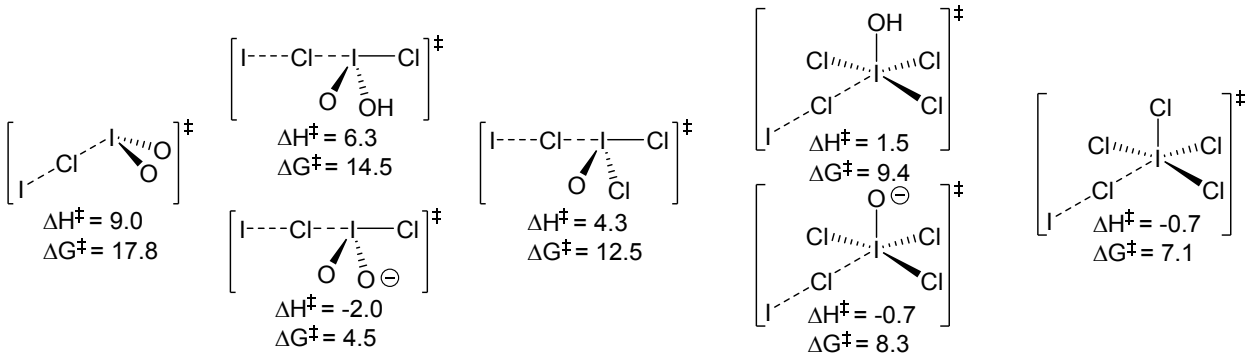
[c]Abbreviations; ax., axial; eq., equatorial; SPy, square pyramidal; SS, see-saw; TPy, trigonal pyramidal. Oxo refers to any terminal bare oxygen atom, without regard to formal charge.

Scheme S2. The lowest energy I(V) species in basic TFAH/H_2O solution with at least one chloro ligand, along with the corresponding I-Cl BDE and free energy change in red.[a]



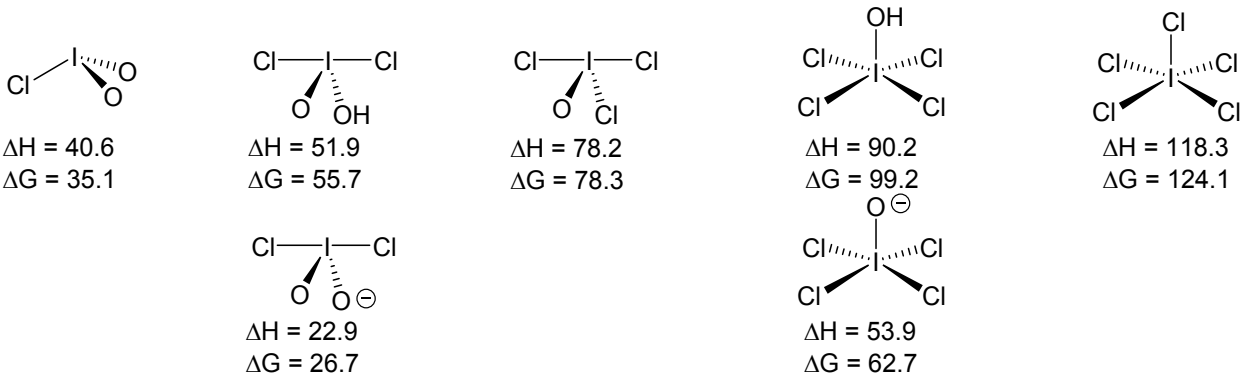
[a]All numbers in kcal/mol. Energies in basic solution are relative to HIO_3, I_2Cl^-, I_2, H_2O, TFAH, and TFA^-.

Figure S1. Transition states associated with the reaction of iodine radical with various I(V) species.[a]



[a]All numbers in kcal/mol and relative to I· and the corresponding I(V) species.

Figure S2. Energies of various I(V)−Cl species in acetic acid solution.[a]



[a]All numbers in kcal/mol and relative to IO_3^-, Cl^-, H_2O, HOAc, and OAc^-.

Scheme S3. The initiation steps for the acidic variation ($(IO_2)_2S_2O_7/Cl^-$ system). All numbers in kcal/mol.

Initiation:

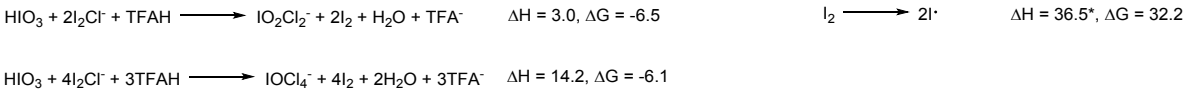


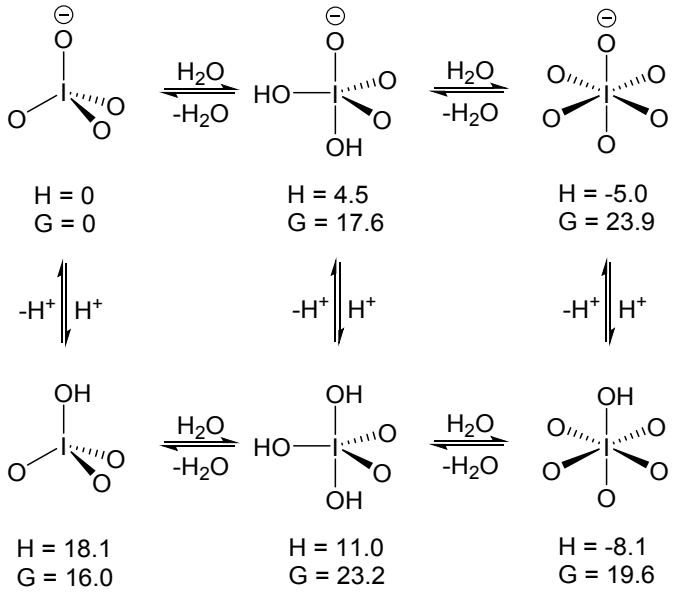
Table S2. Relative enthalpies and free energies of neutral monomeric I(III) species with oxo, hydroxo, TFA, and chloro ligands[a]

Cl	TFA	Species	H (base[a])	G (base[a])	H (acid[a])	G (acid[a])	Geometry notes[b]
0	0	HIO_2	0	0	0	0	B
		$I(OH)_3$	−7.8	6.1	−7.8	6.1	TS
	1	I(O)TFA	4.9	6.0	4.9	6.0	B
		$I(OH)_2$TFA	−19.5	−3.2	−19.5	−3.2	TS; TFA ax.
	2	$I(OH)(TFA)_2$	−19.9	−0.1	−19.9	−0.1	TS; OH eq.
	3	$I(TFA)_3$	−9.9	12.1	−9.9	12.1	TS
1	0	IOCl	7.4	−4.8	4.1	−8.1	B
		$I(OH)_2Cl$	−6.7	−5.7	−9.9	−8.9	TS; Cl ax.
	1	I(OH)ClTFA	−11.6	−7.5	−14.9	−10.8	TS; OH eq.
	2	$ICl(TFA)_2$	−5.5	0.9	−8.7	−2.3	TS; Cl eq.
2	0	$I(OH)Cl_2$	−2.0	−13.2	−8.6	−19.7	TS; OH eq.
	1	ICl_2TFA	2.6	−6.9	−4.0	−13.4	TS; TFA ax.
3	0	ICl_3	6.7	−15.6	−3.1	−25.5	TS

[a]All numbers in kcal/mol. Energies in basic solution are relative to HIO_2, I_2Cl^-, I_2, H_2O, TFAH, and TFA^-. Energies in acidic solution are relative to HIO_2, I_2Cl^-, I_2, H_2O, TFAH, H_2SO_4, and HSO_4^-.

[b]Abbreviations; ax., axial; eq., equatorial; B, bent; TS, T-shaped. Oxo refers to any terminal bare oxygen atom, without regard to formal charge.

Scheme S4. Energetics of the periodate ion with respect to protonation and H_2O adduct formation. All energies in kcal/mol.[a]



[a]"H^+" is shorthand for "+TFAH, −TFA^-".

Table S3. Mulliken charges *q* of different moieties in CX_nH_{4-n} and $[X_nCH_{3-n}$---H---Y]·‡

Description	*n*	X	Y	*q* on C[a]	*q* on H/Cl/O[b]	*q* on Cl/TFA[c]	*q* on Y
CH_4	0	–	–	−0.60317	0.15079	–	–
CH_3TFA[d]	1	TFA	–	−0.32668	−0.13838	−0.26596	–
CH_3Cl	1	Cl	–	−0.40257	−0.11629	–	–
CH_2Cl_2[e]	2	Cl	–	−0.42052	−0.00527	−0.00540	–
$[CH_3$---H---Cl]·‡	0	–	Cl	−0.52426	0.20704	–	−0.22390
$[CH_3$---H---Br]·‡	0	–	Br	−0.50631	0.19425	–	−0.26724
$[TFACH_2$---H---Cl]·‡	1	TFA	Cl	−0.33545	−0.05073	−0.15883	−0.17624
$[TFACH_2$---H---Br]·‡	1	TFA	Br	−0.38721	−0.01643	−0.07393	−0.26691
$[ClCH_2$---H---Cl]·‡	1	Cl	Cl	−0.40838	0.09624	–	−0.22787
$[Cl_2CH$---H---Cl]·‡	2	Cl	Cl	−0.45475	0.15840	0.15847	−0.19116

[a]Charge on carbon of the methane/methyl/methylene moiety.

[b]Charge on electronegative heteroatom attached to carbon (either Cl or O from TFA), or hydrogen if none.

[c]Charge on additional Cl if exists, or entire TFA moiety if exists.

[d]Example: For CH_3TFA species, the "*q* on H/Cl/O" column reports the Mulliken charge on the O attached to the C, and the "*q* on Cl/TFA" column reports the Mulliken charge on the other Cl or the sum of charges on the TFA moiety as a whole.

[e]Example: For CH_2Cl_2 species, the "*q* on H/Cl/O" and "*q* on Cl/TFA" columns report the Mulliken charges on each spectator Cl.

Table S4. Comparison of calculated and experimental enthalpies of reaction

Reaction (all species 1 atm)	Exp ΔH (kcal/mol)	Calc ΔH (kcal/mol)
$I_2 \rightarrow 2I\cdot$	36.5	37.2
$I\cdot + CH_4 \rightarrow HI + CH_3\cdot$	31.7	31.4
$CH_3\cdot + I_2 \rightarrow CH_3I + I\cdot$	-19.0	-20.6
$ICl \rightarrow I\cdot + Cl\cdot$	51	53.0
$Cl\cdot + CH_4 \rightarrow HCl + CH_3\cdot$	-0.2	-0.6
$CH_3\cdot + ICl \rightarrow CH_3Cl + I\cdot$	-30.0	-34.2